Correlations in Short-Term Variations in Atmospheric Oxygen and Carbon Dioxide at Mauna Loa Observatory

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Since January 1991, SIO has measured atmospheric O_2 and CO_2 from flask samples collected by station personnel at MLO at roughly 2-week intervals. Samples were collected in triplicate in 5-L glass flasks, which were flushed overnight and closed off the next day, then shipped back to La Jolla where they were analysed for O_2 and CO_2 concentrations. The results of this program, from January 1991 through to the end of 1993, are shown in Figure 1.

Keeling and Shertz [1992] and *Keeling et al.* [1993] have discussed various aspects of these O_2/N_2 and CO_2 data, including reasons for the observed seasonal cycles in both CO_2 and O_2/N_2; the larger seasonal amplitude in O_2/N_2 than CO_2; the interannual decrease in O_2/N_2; and the resultant implications of these phenomena to the global carbon cycle. In 1992, after slightly more than 1 year of data had been collected, *Keeling and Shertz* [1991] pointed out that there appeared to be greater relative short-term variability in O_2/N_2 at MLO than at other sites, but were unsure of the cause. This paper will try to establish whether the residuals of the flask data from the smooth curves fitted through the data are due to experimental artifacts or real atmospheric variability; that is, whether there is some problem with the sampling procedure used to collect the air samples at MLO or whether there are one or more natural processes affecting the air at MLO, and in a manner not seen at other SIO stations.

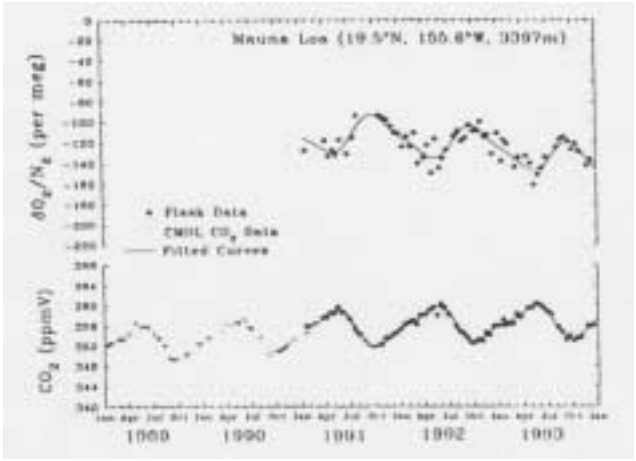

Fig. 1. Measurements of $d(O_2/N_2)$ and CO_2 from air samples collected at Mauna Loa. O_2 concentration changes are reported as changes in the O_2/N_2 ratio of the air sample. We report this ratio relative to a reference as:

$$\delta(O_2/N_2) = \left(\frac{(O_2/N_2)_{sample}}{(O_2/N_2)_{reference}} - 1 \right),$$

and multiply this by 10^6 and express the result in units of "per meg". In these units, 4.8 per meg is equivalent to 1 ppmV. Flask concentrations for a given date (usually three flasks per date) were averaged resulting in a single concentration for each sample date. The scale of the axes were adjusted in such a way that visually, differences in CO_2 can be directly compared with differences in O_2 on a mole fraction basis. For CO_2, supplementary data from CMDL flasks are shown going back to 1989, with some overlap when the sampling program first began. The curves shown (from which all residuals are calculated) were calculated with a least-squares fit to a function of two harmonics (annual and semi-annual periodicity) and a stiff Reinsch spline.

The sampling procedure at MLO is slightly different from that at our other sites. Because samples are collected at an altitude of about 3400 m, a back pressure regulator is used to ensure that our flask samples are pressurized to 760 torr, consistent with samples collected at our sea-level sites. Despite this procedural difference, however, we have found evidence to suggest that a significant fraction of the short-term variability in O_2/N_2 at MLO is due to real atmospheric variability.

This evidence comes from looking at short-term covariations in O_2/N_2 and CO_2. As a measure of short-term variability, we have computed the residuals in O_2/N_2 and CO_2 relative to smooth curves through the data. The curves consist of a two-harmonic fit to account for seasonality and a stiff, *Reinsch* [1967] spline to account for interannual variations. A correlation plot of these residuals is shown in Figure 2, and although there is some scatter, a clear negative correlation can be seen. Statistically speaking, the linear least-squares fit line shown gives an r^2 value of 0.37; thus a minimum of 37% of the variance in the O_2/N_2 residuals can be explained by the variance in the CO_2 residuals. The probability of these data being a random collection of points, and still resulting in an r^2 of 0.37, is less than 0.001.

This statistically significant correlation between O_2/N_2 and CO_2 could either be caused by real atmospheric variations in O_2/N_2 and CO_2, or by systematic flask sampling problems which are influencing both O_2/N_2 and CO_2 simultaneously. This latter possibility can be eliminated by a comparison of our CO_2 data with concurrent data measured by a continuous infrared CO_2 analyzer at MLO operated by C.D. Keeling's group. We calculated residuals of the steady CO_2 data obtained from that instrument relative to the same smooth curves that are fitted to our CO_2 data and correlated those residuals with our own CO_2 residuals. This correlation resulted in an r^2 value of 0.78, showing that almost 80% of the variability in our CO_2 data was also seen in the C.D. Keeling data, hence suggesting that most of the short-term variability in our CO_2 data is due to real atmospheric variations.

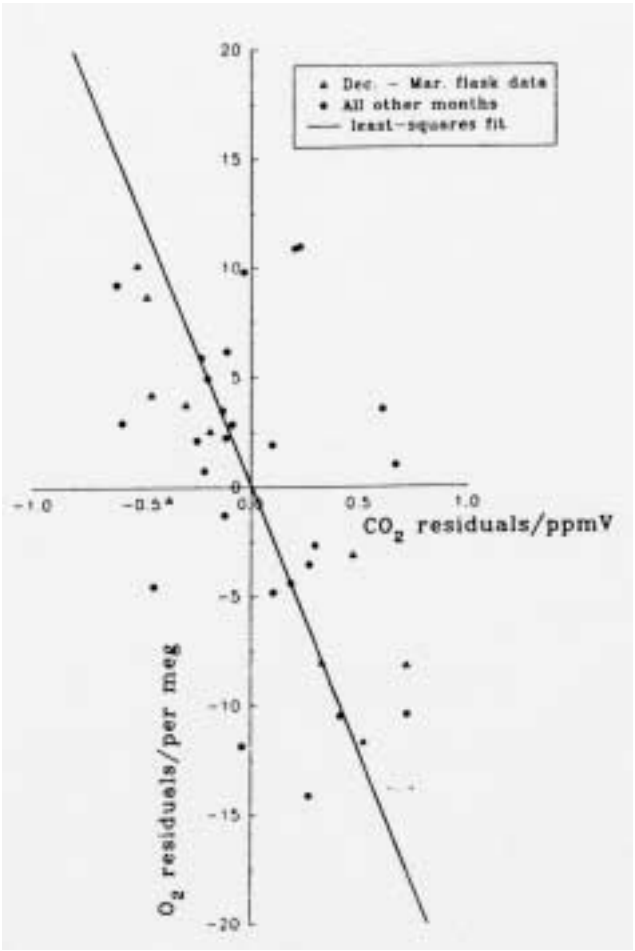

Fig. 2. CO_2 and O_2/N_2 residuals of the flask data from the smooth curves of Figure 1 are shown plotted against each other. Samples were included only if they were collected during a period of steady CO_2 concentration, as defined by C.D. Keeling's group using their continuous CO_2 analyzer at MLO; as a result only 37 sampling dates, from an original 59, were used. A clear negative correlation can be seen.

Additionally, a correlation of our O_2/N_2 data with C.D. Keeping's CO_2 data produced an r^2 value of 0.36. This is almost identical to the correlation with our own CO_2 data that had the advantage of being taken from the same flask samples as the O_2/N_2 data.

Having shown that a significant fraction of the short-term variability in O_2/N_2 and CO_2 at MLO is due to atmospheric changes, we now ask the question: what may be causing these background variations? *Heimann et al.* [section 5.5, 1989] have shown that a significant fraction of the CO_2 variability at MLO is related to changing synoptic weather patterns in the area. Particularly important may be variations in north-south transport, since for much of the year, due to both seasonal and anthropogenic differences, air masses to the north of MLO have large differences in O_2/N_2 and CO_2 concentrations relative to air masses to the south. *Keeling, et al.* [section 2, 1989] have also shown that the zonal mean CO_2 concentration at the latitude of MLO is almost identical to the actual CO_2 concentration measured at MLO, hence further suggesting that longitudinal variations are not as important as north-south variations. Although there is no direct measurement of these north-south gradients at MLO, their magnitude can be estimated based on the differences in O_2/N_2 and CO_2 that exist between midlatitude sites in each hemisphere; La Jolla, California, at 32.9°N, and Cape Grim, Tasmania, at 40.7°S. Curves for these sites are shown in Figure 3.

If variations in north-south transport are in fact causing the short-term variability at MLO, then we would expect the ratio of the instantaneous O_2/N_2 and CO_2 gradients (shown in Figure 3) to be roughly equal to the ratio of the short-term covariations in O_2/N_2 and CO_2. In other words, we would expect the ratio of the two vertical lines shown in Figure 3 to be roughly equal to the slope of the envelope of the flask residuals shown in Figure 2, for the same time period. In the period from December through March, when the ratio of the north-south gradient is at its most stable, the average absolute value of this north-south O_2/N_2 versus CO_2 ratio is 15 ± 3 per meg $ppmV^{-1}$, while a least squares fit to the flask residuals over this period results in a slope of 17 ± 4 per meg $ppmV^{-1}$. This agreement suggests that the north-south transport may indeed be implicated as a source of variability at MLO. However, this analysis is hardly conclusive because we have only 3 years worth of data to work with, and we are close to the level of our experimental uncertainty. Also, the rapid seasonal variations in the interhemispheric gradient complicates the analysis.

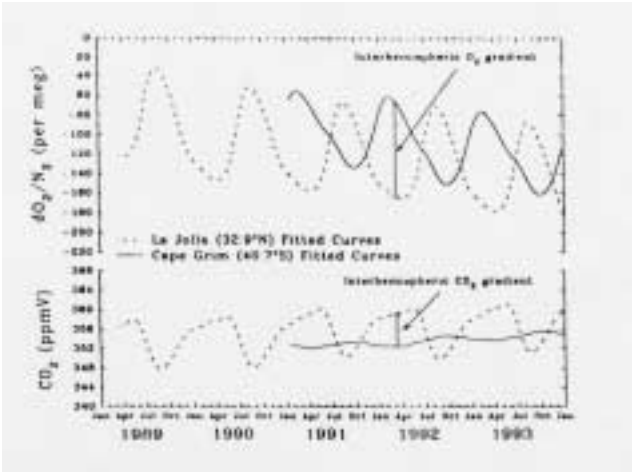

Fig 3. Seasonal patterns of O_2/N_2 and CO_2 as observed at La Jolla, California, and Cape Grim, Tasmania, Australia. The curves are fits to flask data (not shown) similar to those shown in Figure 1 for MLO, except that the seasonality is represented here by four harmonics instead of two. The difference between O_2/N_2, and CO_2 concentrations at these two sites can be taken as a measure of the interhemispheric gradient between the middle latitudes in the northern and southern hemispheres. The vertical lines show examples of the north-south gradient in O_2/N_2 in the top plot, and CO_2 in the bottom plot. These gradients change rapidly with time, due to opposing seasonal changes in the two hemispheres.

In conclusion, we have shown that a significant fraction of the short-term variability in our CO_2 and O_2/N_2 data at MLO can be explained by real atmospheric variability rather than by artifacts of our flask sampling procedure or analysis. We have suggested that this variability may be related to seasonal north-south concentration gradients that exist in the tropics as a result of opposing seasonal variations at middle latitudes in either hemisphere and have given statistical evidence to support this. If we are correct, we would expect to see high variability at other tropical sites as well. We have recently started collecting flask samples at two additional tropical sites supported by NOAA personnel, one at Cape Kumukahi, also in Hawaii, but at sea level, and another in American Samoa, at a latitude of 14.3°S. The Cape Kumukahi site should help to eliminate the parameter of variable altitude, which can have an effect on results obtained, as shown for CO_2 in *Keeling et al.*, [section 2, 1989]. These new sites, along with the continuing MLO data should, over time, help to clarify the interpretations put forward in this paper.

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